

## Chemistry

### Lecture 17

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## Electrochemistry

### Outline:

- ✚ Oxidation number of Elements
- ✚ Explanation of Electrolysis
- ✚ Standard electrode potential
- ✚ Standard Hydrogen electrode
- ✚ Balancing redox equation by oxidation number change method
- ✚ Balancing redox equation by ion-electron method

### Electrochemistry

- ◆ Electrochemistry is concerned with the conversion of electrical energy into chemical energy as well as the conversion of chemical energy into electrical energy

### Redox Reactions

- ❖ Reaction which involve transfer of electrons from one specie to another
- ❖ Electron transfer reactions
- ❖ Oxidation and reduction take place simultaneously

Reducing Agent	Oxidizing Agent
Also called Reductant	Also called Oxidant
Reduces others but <b>Self oxidizes</b>	Oxidizes others but self reduces
Oxidation (loss of H/loss of electron or gain of O) (electron donor)	Reduction (gain of H/gain of electron or loss of O) (electron acceptor)
Oxidation number increases $\text{Na}^0 \rightarrow \text{Na}^{+1} + 1\text{e}^-$ O.N (0 $\rightarrow$ +1)	Oxidation number decreases $\text{Cl}^0 + 1\text{e}^- \rightarrow \text{Cl}^{-1}$ O.N (0 $\rightarrow$ -1)
<b>Examples:</b> Metals, $\text{H}_2\text{S}$ , $\text{HF/HBr/HCl/HI}$ , $\text{CO}$ , $\text{FeSO}_4$ , $(\text{COOH})_2$ , $\text{KI}$	<b>Examples:</b> Non-metals, $\text{F}_2/\text{Br}_2/\text{Cl}_2/\text{I}_2$ , $\text{CO}_2$ , $\text{O}_2$ , $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ , $\text{KMnO}_4$ , $\text{K}_2\text{Cr}_2\text{O}_7$ , etc
<b>Note; If O.N of central atom is equal to its group number then such substance always act as oxidizing agent i.e. <math>\text{CO}_2</math> (C = +4), <math>\text{HNO}_3</math> (N = +5) etc</b>	

### Oxidation Number/State (O.N)

- ☞ Apparent charge on an atom in a molecule. It can be **zero, positive** or **negative**

### Rules:

- O.N in free state is zero i.e.  $H_2^0$ ,  $Na^0$
- O.N of neutral molecule/compound is equal to zero.
- O.N of group IA (+1), IIA (+2), IIIA (+3)
- O.N of hydrogen (+1) except metal hydrides (-1)
- O.N of oxygen in normal oxides (-2), peroxides (-1), super oxides (-1/2) and in sub oxide i.e.  $OF_2$  (+2)
- O.N of more E.N atom is negative
- In ions, algebraic sum of O.N is equal to charge on ion.
- Short cut (1) In  $SO_4^{2-}$  S has O.N = +6 (2) In  $NO_3^{1-}$  N has O.N = +5

#### Practice Q.4 (c), (d)

$KMnO_4$ $K + Mn + 4(O) = 0$ $+1 + Mn + 4(-2) = 0$ $+1 + Mn - 8 = 0$ $Mn - 7 = 0$ $Mn = +7$	$NO_3^{1-}$ $N + 3(O) = -1$ $N + 3(-2) = -1$ $N - 6 = -1$ $N = -1 + 6$ $N = +5$
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### Balancing of Equation by Redox Method (see handouts)

#### Rules (For concept only): (Q.5)

- ❖ Write down the skeleton of the equation
- ❖ Identify the elements undergoing change in oxidation state
- ❖ If single element shows two dissimilar O.S in product, then add same molecule containing that element on left side of the equation
- ❖ Identify the number of electrons lost during oxidation
- ❖ Identify the number of electrons gained during reduction
- ❖ Equate the number of electrons lost and gained by multiplying with suitable digit
- ❖ Oxidation and reduction parts will be multiplied with those digits, used for equating the electrons respectively
- ❖ **Note: Inspection method isn't applied on parts balanced by redox method**

**Example:**  $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$  (Practice solution applying rules given above)

**Cu oxidizes from 0  $\rightarrow$  +2, N reduces from +5  $\rightarrow$  +4, Cu (reducing agent), N (oxidizing agent)**

### Balancing of Equation by ion-electron method (see handouts)

**Electrolysis:** Electrochemical reactions that occur at electrodes during the electrolytic conduction. Specially devised cell is used for this process. The ions of electrolyte go to respective electrode and undergo redox reactions

Or

Decomposition of a substance (molten/aqueous) in presence of electricity and the substance is called **Electrolyte**

**Hydrolysis:** Decomposition of substance in presence of water

**Pyrolysis:** Decomposition of a substance in presence of heat

**Electrolytic Conduction:** Movement of ions/charges through liquid by application of electricity in Electrolytic cell

**Cell:** Consists of two electrodes i.e. anode and cathode

**Battery:** Combination of cells

**Electrodes:** Metallic or non-metallic surface on which the redox reaction occurs

- ✓ **Inert Electrodes:** Do not take part in reaction i.e. Pt, graphite
- ✓ **Reactive Electrodes:** Undergo chemical change i.e. Zn, Cd etc

<b>Anode</b>	<b>Cathode</b>
Electrons leave the cell through anode	Electrons enter the cell through cathode
Represented with longer line	Represented with smaller line
Usually shown on left side of the cell	Usually shown on right side of the cell
Oxidation takes place on it	Reduction takes place on it
So standard oxidation potential develops	So standard reduction potential develops
Shown with +ve sign in Electrolytic cell	Shown with –ve sign in Electrolytic cell
Shown with –ve sign in Galvanic cell	Shown with +ve sign in Galvanic cell
In galvanic cell, reactive anode can consume as result of it oxidation and cell will stop working if happens so	In galvanic cell, mass of cathode increases as result of reduction (result of deposition)

#### Electrochemical Cells:

<b>Galvanic/Voltaic Cell</b>	<b>Electrolytic Cell</b>
Chemical energy converted to electrical energy	Electrical energy converted to chemical energy
Spontaneous redox reactions occur	Non-Spontaneous redox reactions occur
Salt bridge is used if two electrolytes are used	Salt bridge never used
Two half cells are placed in separate containers	Both electrodes in placed in same cell
Electric current moves from anode to cathode	Electric current supplied through battery enters cell through the cathode
Example: Daniel cell(Zn-Cu), Dry alkaline cell etc	Example: Down's cell, Nelson's cell etc

## Electrolysis of Electrolytes and substances Liberated at Electrodes

☐ In molten there is no problem as only one kind of ion goes to respective electrode and get deposited  $\text{PbCl}_{2(s)} \rightarrow \text{Pb}_{(l)}^{+2} + 2\text{Cl}_{(l)}^{-}$

☐ In case aqueous solutions of salts, more than one kind of ions can go to each electrode due to ionization of water, so we follow order given in the table. For example



Deposition of +ve ions at Cathode	Deposition of –ve ions at Anode
Greater the $E_{\text{red}}^0$ , more will be deposition Ease of deposition increases down the table	$\text{I}^- > \text{Br}^- > \text{OH}^- > \text{Cl}^- > \text{NO}_3^{-1} > \text{SO}_4^{-2}$ ( $\text{OH}^- > \text{Cl}^-$ only when very dilute solutions of chlorides salts) ( $\text{OH}^- < \text{Cl}^-$ when conc. solutions of chlorides salts)
$\text{Li}^+ < \text{Ca}^{+2} < \text{Mg}^{+2} < \text{Zn}^{+2} < \text{Pb}^{+2} < \text{H}^+ < \text{Cu}^+ < \text{Ag}^+$	

Electrolyte	Cathode	Anode
$\text{PbBr}_{2(\text{molten})}$	$\text{Pb(s)}$	$\text{Br}_{2(\text{g})}$
$\text{NaCl}_{(\text{molten})}$	$\text{Na(s)}$	$\text{Cl}_{2(\text{g})}$
$\text{NaCl(aq)}$	$\text{H}_{2(\text{g})}$	$\text{Cl}_{2(\text{g})}$
$\text{CuCl}_{2(\text{aq})}$	$\text{Cu(s)}$	$\text{Cl}_{2(\text{g})}$
$\text{CuSO}_4(\text{aq})$	$\text{Cu(s)}$	$\text{O}_{2(\text{g})}$
$\text{KNO}_3(\text{aq})$	$\text{H}_{2(\text{g})}$	$\text{O}_{2(\text{g})}$
$\text{NaOH(aq)}$	$\text{H}_{2(\text{g})}$	$\text{O}_{2(\text{g})}$
$\text{H}_2\text{SO}_4(\text{aq})$	$\text{H}_{2(\text{g})}$	$\text{O}_{2(\text{g})}$

### Electrolytic Processes of Industrial Importance:

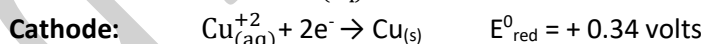
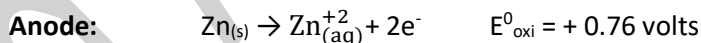
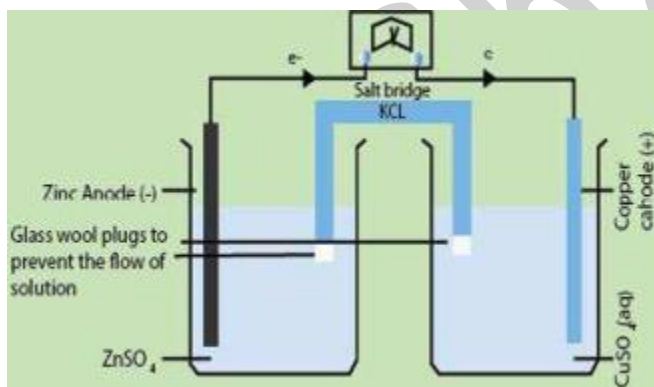
- Extraction of sodium by the electrolysis of fused sodium chloride is carried out in Down's cell  
At Anode (graphite):  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   
At Cathode (iron):  $2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}$
- Caustic soda is obtained on industrial scale by the electrolysis of concentrated aqueous solution of sodium chloride in Nelson cell and Castner- Kellner cell (Hg- cell)  
At Anode (Titanium):  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$   
At Cathode (Mercury or steel):  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$   
 $2\text{Na}^+ + 2\text{OH}^- \rightarrow 2\text{NaOH}$
- Magnesium and calcium metals are extracted by the electrolysis of their fused chlorides. Mg and Ca are collected at cathodes while  $\text{Cl}_2$  at anodes
- Aluminium is extracted by electrolyzing fused bauxite,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  in the presence of fused cryolite,  $\text{Na}_3\text{AlF}_6$  (lowers M.P). This process is called Hall-Beroult process
- Anodized aluminium is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid, which coats a thin layer of oxide on it

- Electrolytic cell can also be used for the purification of copper. Impure copper is made the anode and a thin sheet of pure copper is made the cathode. Copper sulphate solution is used as an electrolyte. The atoms of Cu from impure Cu anode are converted to  $\text{Cu}^{2+}$  ions and migrate to cathode which is made up of pure Cu.
- Copper, silver, nickel and chromium plating is done by various types of electrolytic cells. One metal is deposited at the surface of another metal

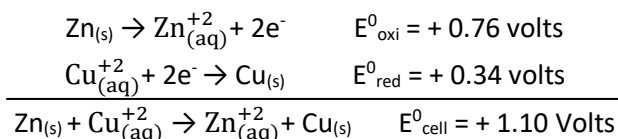
## Galvanic Cell

### Example: Zn-Cu cell

- Zn being higher than Cu in electrochemical series acts as anode and Cu acts as cathode
- Oxidation occurs at Zn and reduction on Cu
- Flow of electrons is from Zn to Cu



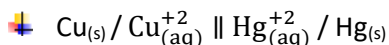
- ✓ As we know ( $E^0_{\text{cell}} = E^0_{\text{red}} + E^0_{\text{oxi}}$ ), so add two reactions occurring at both electrodes



### Cell Representation;



- ✓ Write following in reaction form;

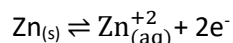


## Electrode Potential and Cell Potential

Electrode Potential (E)	Standard Electrode Potential ( $E^0$ )	Standard Cell Potential ( $E^0_{\text{cell}}$ )
The potential set up when an electrode is in contact with solution of its own ions	The potential set up when an electrode is in contact with 1M solution of its own ions at 298K 'T' and 1 atm 'P'	The force with which electrons move in a circuit, therefore measure the tendency of cell reaction to occur

It is measured for any concentration of solution at any 'T' and 'P'	Measured under standard conditions i.e. 1M solution, 298k 'T' and 1 atm P'	Galvanic cell thus gives quantitative measures of relative tendency of various reactions to occur
We cannot measure the potential directly. But we can measure the difference in potential between the metal/metal ion system and another system		$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{oxi}}$
-----	Measured in form of $E^{\circ}_{\text{red}}$ (tendency to gain $e^{-}$ ) or $E^{\circ}_{\text{oxi}}$ (tendency to lose $e^{-}$ )	It is also termed as Electromotive (emf) force of cells

- ☞ When a zinc rod is placed in contact with an aqueous solution of its ions, the following equilibrium exists;

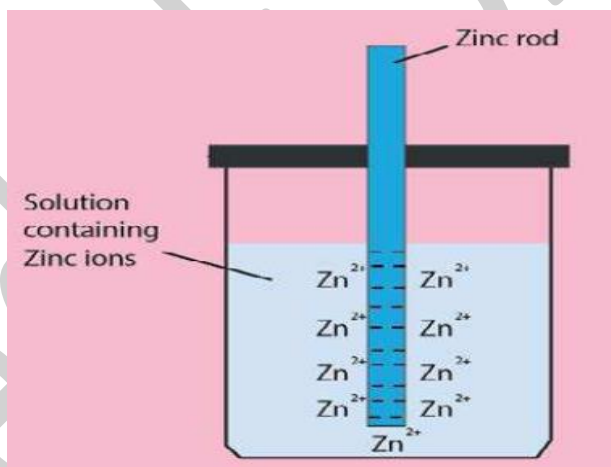


- ☞ There are two opposing reactions in this equilibrium;

- Metal atoms from the rod entering the solution as metal ions. This leaves electrons behind on the surface of the rod  

$$\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{+2}_{(\text{aq})} + 2e^{-}$$
- Ions in solution accepting electrons from the metal rod and being deposited as metal atoms on the surface of the rod  

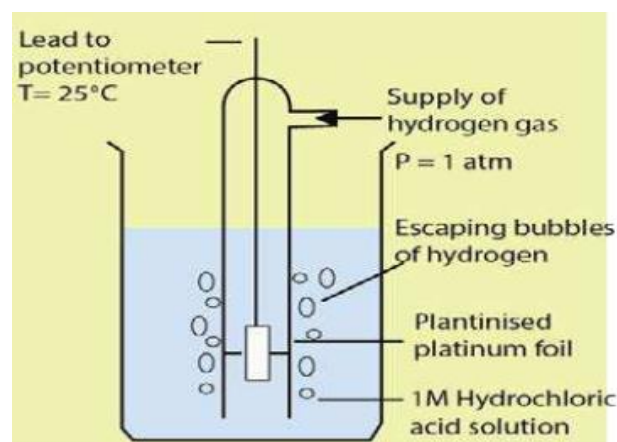
$$\text{Zn}^{+2}_{(\text{aq})} + 2e^{-} \rightarrow \text{Zn}_{(\text{s})}$$
- The redox equilibrium is established when the rate of electron gain equals the rate of electron loss



- ☞ For metal less reactive this equilibrium as compared to the equilibrium set up by other more reactive metals, lies further over to the left (more atoms) i.e. gain of electrons and deposit of metal on electrode ( $\text{Cu}^{+2}_{(\text{aq})} + 2e^{-} \rightarrow \text{Cu}_{(\text{s})}$ )
- ☞ For more reactive metals this equilibrium as compared to the equilibrium set up by other less reactive metals, lies further over to the right (more ions) i.e. loss of electrons and dissolution of metal on electrode ( $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{+2}_{(\text{aq})} + 2e^{-}$ )

### Standard Hydrogen Electrode

- ☞ It consists of a piece of platinum foil, which is coated electrolytically with finely divided platinum black, to give it a large surface area



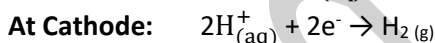
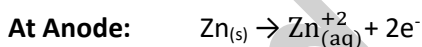
- ▣ The platinum (inert electrode) acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution
  - ▣ The potential of this electrode is arbitrarily taken as zero
  - ▣ Reference electrode [other can be Calomel electrode (Hg coated with  $\text{Hg}_2\text{Cl}_2$  and KCl electrolyte) more easy to use]
  - ▣ Can act as anode as well cathode depending on other electrode attached to it
- As Anode** with electrodes of **high  $E^\circ_{\text{red}}$**  (Cu, Ag etc)       $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+_{(\text{aq})} + 2\text{e}^-$
- As Cathode** with electrodes of **low  $E^\circ_{\text{red}}$**  (Zn, Cd etc)       $2\text{H}^+_{(\text{aq})} + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$

### Measurement of Electrode Potentials of Metals

- ◆ Metal electrode is connected electrolytically with SHE to establish Galvanic cell

#### For Zinc (Zn):

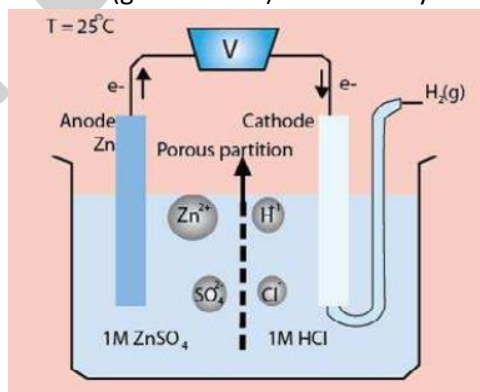
- ◆ Zn when connected with SHE loses electrons easily therefore acts as anode
- ◆ Deflection in voltmeter shows that Zn has greater tendency to lose electrons (get oxidized) than SHE by 0.76 volts
- ◆ Therefore  $E^\circ_{\text{oxi}}$  for Zn = + 0.76 volts
- ◆ That also means Zn will have lesser tendency to gain electrons (get reduced) than SHE by 0.76 volts
- ◆ Therefore  $E^\circ_{\text{red}}$  for Zn = - 0.76 volts
- ◆  $E^\circ_{\text{oxi}} = E^\circ_{\text{red}}$  (have different sign)
- ◆ Flow of electrons is from Zn to SHE



- ◆ Both the electrolytes are separated by salt bridge

#### ❖ Salt Bridge:

- ☞ Salt bridge contains electrolyte usually aqueous solution of KCl with agar-agar (red algae) paste
- ☞ Other electrolytes i.e.  $\text{KNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  etc can also be used
- ☞ Function of salt bridge is to;
  - Keep two electrolytes separated
  - Maintain electrical neutrality by diffusing +ve and -ve ions into required half cells
  - Keeps the flow of current going in circuit (if not present, voltage drops to zero)

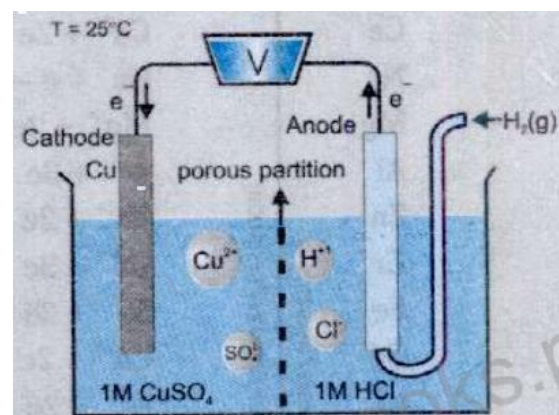


#### For Copper (Cu):

- ◆ Cu when connected with SHE gains electrons easily therefore acts as cathode
- ◆ Deflection in voltmeter shows that Cu has greater tendency to gain electrons (get reduced) than SHE by 0.34 volts



- ◆ Therefore  $E^0_{\text{red}}$  for Cu = + 0.34 volts
- ◆ That also means Cu will have lesser tendency to lose electrons (get oxidized) than SHE by 0.34 volts
- ◆ Therefore  $E^0_{\text{oxi}}$  for Cu = - 0.34 volts
- ◆  $E^0_{\text{oxi}} = E^0_{\text{red}}$  (have different sign)
- ◆ Flow of electrons is from SHE to Cu
  - At Anode:**  $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+_{(\text{aq})} + 2\text{e}^-$
  - At Cathode:**  $\text{Cu}^{+2}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Cu}_{(\text{s})}$
- ◆ Both the electrolytes are separated by salt bridge



### Electrochemical Series

- When elements are arranged in the order of their standard, electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series
- Values in the table are of  $E^0_{\text{red}}$  of different species

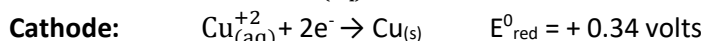
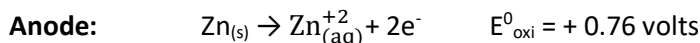
Element	Electrode	Standard Reduction Potential ( $E^0$ )
Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.045
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126
$\text{H}_2$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	(Reference Electrode) 0.000
Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
Cu	$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	+0.521
$\text{I}_2$	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.535
Fe	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	+0.771
Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.7994
Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.885
$\text{Br}_2$	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.08
$\text{Cl}_2$	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.360
Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50
$\text{F}_2$	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87



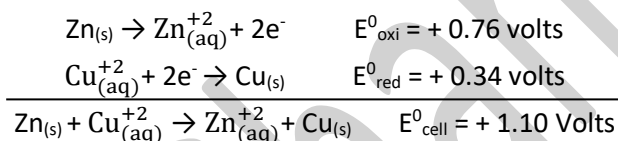
➤ **Applications: [As only concept & as precaution]**

**i. Calculation of Standard Cell Potential ( $E^0_{\text{cell}}$ ) or *emf* :**

- In electrochemical series an electrode occupying higher position than the other will act as anode
- In electrochemical series an electrode occupying lower position than the other will act as cathode



- ✓ As we know ( $E^0_{\text{cell}} = E^0_{\text{red}} + E^0_{\text{oxi}}$ ), so add two reactions occurring at both electrodes



**ii. Feasibility of a Chemical Reaction:**

- ☞ For a reaction to be feasible (spontaneous),  $E^0_{\text{cell}}$  must be positive
- ☞  $\text{Zn}_{(\text{s})} + \text{Cu}^{+2}_{(\text{aq})} \rightarrow \text{Zn}^{+2}_{(\text{aq})} + \text{Cu}_{(\text{s})}$  is feasible as value of  $E^0_{\text{cell}} = + 1.10 \text{ Volts}$

**iii. Tendency of Metals or Non-metals to get Oxidized or Reduced:**

- ☞ Metals undergo oxidation (act as reducing agents) and non metals undergo reduction (act as oxidizing agents)
- ☞  $E^0_{\text{red}} \propto \frac{1}{\text{Ease of Oxidation}}$   $E^0_{\text{red}} \propto \frac{1}{\text{Reducing Power}}$
- ☞  $E^0_{\text{red}} \propto \text{Ease of Reduction}$   $E^0_{\text{red}} \propto \text{Oxidizing Power}$
- ☞ Li at top of the table is strongest reducing agent (it has lowest  $E^0_{\text{red}}$ ) and  $\text{F}_2$  at bottom of table is strongest oxidizing agent (it has highest  $E^0_{\text{red}}$ )

**iv. Relative Chemical Reactivity of Metals:**

- ☞ Smaller the reduction potential of a metal, greater will be its reactivity
- ☞ Li, Na, K, Ca etc are most reactive metals due to low reduction potential values
- ☞ Coinage metals are least reactive due to positive values of reduction potential

**v. Reaction of Metals with Dilute Acids: (displacement reaction)**

- ☞ Lower the reduction potential value for metal, easier is for it to remove  $\text{H}_2$  gas from acids
- ☞ Metals like Ag, Au, Pt, Cu cannot displace  $\text{H}_2$  gas from acid

**vi. Displacement of one Metal by another Metal from its solution:**

- ☞ Metal which lies above (low reduction potential) than other metal can displace that other metal (lie below) from its solution
- ☞ Zn can displace Cu from  $\text{CuSO}_4$  but not Mg from  $\text{MgSO}_4$
- ☞ **Non-metal:** In case of non metals, non-metal with high reduction potential can displace other non-metal with low reduction potential from its compounds
- ☞  $\text{F}_2$  can displace all other halogens,  $\text{Cl}_2$  can displace  $\text{Br}_2$  and  $\text{I}_2$  but cannot displace  $\text{F}_2$